US009067855B2

(12) **United States Patent**
Grandbois et al.

(10) **Patent No.: US 9,067,855 B2**
(45) **Date of Patent: Jun. 30, 2015**

(54) **PROCESS FOR THE PRODUCTION OF CHLORINATED ALKANES**

(71) Applicants: **Matthew L. Grandbois**, Midland, MI (US); **William J. Kruper, Jr.**, Sanford, MI (US)

(72) Inventors: **Matthew L. Grandbois**, Midland, MI (US); **William J. Kruper, Jr.**, Sanford, MI (US)

(73) Assignee: **Dow Global Technologies LLC**, Midland, MI (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **14/358,079**

(22) PCT Filed: **Nov. 13, 2012**

(86) PCT No.: **PCT/US2012/064792**

§ 371 (c)(1),
(2) Date: **May 14, 2014**

(87) PCT Pub. No.: **WO2013/078035**

PCT Pub. Date: **May 30, 2013**

(65) **Prior Publication Data**

US 2015/0045592 A1 Feb. 12, 2015

Related U.S. Application Data

(60) Provisional application No. 61/562,025, filed on Nov. 21, 2011.

(51) **Int. Cl.**
C07C 17/013 (2006.01)
C07C 17/10 (2006.01)

(52) **U.S. Cl.**
CPC ***C07C 17/013*** (2013.01); ***C07C 17/10*** (2013.01)

(58) **Field of Classification Search**
CPC C07C 17/013; C07C 17/10
USPC 570/261
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

2,119,484	A	5/1938	Levine
2,179,378	A	11/1939	Metzger
2,207,193	A	7/1940	Groll
2,299,441	A	10/1942	Vaughan
2,302,228	A	11/1942	Kharasch
2,370,342	A	2/1945	Zellner
2,378,859	A	6/1945	Martin
2,435,983	A	2/1948	Schmerling
2,449,286	A	9/1948	Fairbairn
2,588,867	A	3/1952	Morris
2,630,461	A	3/1953	Sachsse
2,688,592	A	9/1954	Skeeters
2,762,611	A	9/1956	Monroe
2,765,359	A	10/1956	Pichler
2,964,579	A	12/1960	Weller et al.
2,973,393	A	2/1961	Monroe
3,000,980	A	9/1961	Asadorian
3,094,567	A	6/1963	Eaker
3,112,988	A	12/1963	Coldren et al.
3,444,263	A	5/1969	Fernald
3,446,859	A	5/1969	Weil
3,502,734	A	3/1970	Baird
3,525,595	A	8/1970	Zirngibl Hans et al.
3,551,512	A	12/1970	Loeffler
3,558,438	A	1/1971	Schoenbeck
3,651,019	A	3/1972	Asscher
3,676,508	A	7/1972	Krekeler
3,819,731	A	6/1974	Pitt
3,823,195	A	7/1974	Smith
3,872,664	A	3/1975	Lohmann
3,914,167	A	10/1975	Ivy
3,926,758	A	12/1975	Smith
3,948,858	A	4/1976	Weirsum
3,954,410	A	5/1976	Pohl
4,038,372	A	7/1977	Colli
4,051,182	A	9/1977	Pitt
4,319,062	A	3/1982	Boozalis et al.
4,513,154	A	4/1985	Kurtz
4,535,194	A	8/1985	Woodard
4,614,572	A	9/1986	Holbrook

(Continued)

FOREIGN PATENT DOCUMENTS

CH	609022	6/1974
CN	101492341	7/2009
CN	101544535	9/2009
CN	101597209	12/2009
CN	101913979	12/2010
CN	101913980	12/2010
CN	101955414	1/2011
CN	101982227	3/2011
CN	102001911	4/2011
CN	102249846	11/2011

(Continued)

OTHER PUBLICATIONS

Bai et al, "Isomerization of Tetrachloropropene to Promote Utilization Ratio of Triallate Raw Materials", Petrochemical Technology & Application, 2007, 25(1).

(Continued)

Primary Examiner — Shailendra Kumar
(74) *Attorney, Agent, or Firm* — Susan M. Zerull; KSJLAW, LLC

(57) **ABSTRACT**

Processes for the production of chlorinated alkanes are provided. The present processes comprise reacting one or more mono- and/or dichloroalkanes to form tri-, tetra- and/or pentachloroalkanes, with high regioselectivity. In those embodiments wherein a dichloroalkane is desirably utilized, it may advantageously be a vicinal dichloroalkane. Further, only one catalyst is utilized. The present processes make use of sulfuryl chloride as a chlorinating agent, rather than a gaseous chlorinating agent such as chlorine gas. Finally, the process uses lower intensity process conditions than at least some conventional processes, and thus, operating costs are saved.

14 Claims, No Drawings

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,644,907	A	2/1987	Hunter
4,650,914	A	3/1987	Woodard
4,661,648	A	4/1987	Franklin
4,702,809	A	10/1987	Mueller
4,714,792	A	12/1987	Muller
4,716,255	A	12/1987	Muller
4,726,686	A	2/1988	Wolf
4,727,181	A	2/1988	Kruper
4,849,554	A	7/1989	Cresswell et al.
4,894,205	A	1/1990	Westerman
4,902,393	A	2/1990	Muller
4,999,102	A	3/1991	Cox
5,057,634	A	10/1991	Webster
5,132,473	A	7/1992	Furutaka
5,171,899	A	12/1992	Furutaka
5,178,844	A	1/1993	Carter et al.
5,254,771	A	10/1993	Cremer
5,254,772	A	10/1993	Dukat
5,254,788	A	10/1993	Gartside
5,262,575	A	11/1993	Dianis
5,315,044	A	5/1994	Furutaka
5,367,105	A	11/1994	Miyazaki et al.
5,414,166	A	5/1995	Kim
5,504,266	A	4/1996	Tirtowidjojo et al.
5,684,219	A	11/1997	Boyce
5,689,020	A	11/1997	Boyce
5,811,605	A	9/1998	Tang
5,895,825	A	4/1999	Elsheikh
5,986,151	A	11/1999	Van Der Puy
6,111,150	A	8/2000	Sakyu
6,118,018	A	9/2000	Savidakis
6,160,187	A	12/2000	Strickler
6,187,976	B1	2/2001	Van Der Puy
6,229,057	B1	5/2001	Jackson et al.
6,235,951	B1	5/2001	Sakyu et al.
6,472,573	B1	10/2002	Yamamoto
6,518,467	B2	2/2003	Tung et al.
6,538,167	B1	3/2003	Brown
6,545,176	B1	4/2003	Tsay
6,551,469	B1	4/2003	Nair
6,610,177	B2	8/2003	Tsay
6,613,127	B1	9/2003	Galloway
6,683,216	B1	1/2004	Zoeller
6,825,383	B1	11/2004	Dewkar
6,924,403	B2	8/2005	Barnes et al.
6,958,135	B1	10/2005	Filippi
7,117,934	B2	10/2006	Lomax
7,189,884	B2	3/2007	Mukhopadhyay
7,226,567	B1	6/2007	Olbert
7,282,120	B2	10/2007	Braun
7,297,814	B2	11/2007	Yada
7,345,209	B2	3/2008	Mukhopadhyay
7,371,904	B2	5/2008	Ma
7,378,559	B2	5/2008	Verwijs
7,396,965	B2	7/2008	Mukhopadhyay
7,511,101	B2	3/2009	Nguyen
7,521,029	B2	4/2009	Guetlhuber
7,588,739	B2	9/2009	Sugiyama
7,659,434	B2	2/2010	Mukhopadhyay
7,674,939	B2	3/2010	Mukhopadhyay
7,687,670	B2	3/2010	Nappa
7,695,695	B2	4/2010	Shin
7,714,177	B2	5/2010	Mukhopadhyay
7,836,941	B2	11/2010	Song
7,880,040	B2	2/2011	Mukhopadhyay
7,951,982	B2	5/2011	Mukhopadhyay
8,058,486	B2	11/2011	Merkel
8,058,490	B2	11/2011	Strebelle
8,071,825	B2	12/2011	Johnson
8,071,826	B2	12/2011	Van Der Puy
8,076,521	B2	12/2011	Elsheikh
8,084,653	B2	12/2011	Tung
8,115,038	B2	2/2012	Wilson
8,123,398	B2	2/2012	Teshima
8,158,836	B2	4/2012	Pigamo
8,232,435	B2	7/2012	Sievert
8,258,353	B2	9/2012	Kruper
8,258,355	B2	9/2012	Merkel
8,357,828	B2	1/2013	Okamoto
8,367,867	B2	2/2013	Zardi
8,383,867	B2	2/2013	Mukhopadhyay
8,395,000	B2	3/2013	Mukhopadhyay
8,398,882	B2	3/2013	Rao
8,487,146	B2	7/2013	Wilson
8,581,011	B2	11/2013	Tirtowidjojo
8,581,012	B2	11/2013	Tirtowidjojo
8,614,361	B2	12/2013	Suzuki
8,614,363	B2	12/2013	Wilson
2001/0018962	A1	9/2001	Joshi
2002/0110711	A1	8/2002	Boneberg
2006/0150445	A1	7/2006	Redding
2006/0292046	A1	12/2006	Fruchey
2007/0197841	A1	8/2007	Mukhopadhyay
2007/0265368	A1	11/2007	Rao
2008/0021229	A1	1/2008	Maughon
2008/0073063	A1	3/2008	Clavenna et al.
2008/0118018	A1	5/2008	Schrauwen
2008/0207962	A1	8/2008	Rao
2009/0018377	A1	1/2009	Boyce
2009/0099396	A1	4/2009	Mukhopadhyay
2009/0117014	A1	5/2009	Carpenter
2009/0203945	A1	8/2009	Mukhopadhyay
2010/0041864	A1	2/2010	Kadowaki et al.
2010/0185029	A1	7/2010	Elsheikh
2010/0263278	A1	10/2010	Kowoll et al.
2011/0172472	A1	7/2011	Sakyu
2011/0218369	A1	9/2011	Elsheikh
2011/0251425	A1	10/2011	Penzel
2012/0065434	A1	3/2012	Nose
2014/0081055	A1	3/2014	Tirtowidjojo

FOREIGN PATENT DOCUMENTS

CN	102351637		2/2012
DE	857955		12/1952
DE	209184		4/1984
DE	235631		5/1986
DE	102005044501		3/2007
DE	102010022414		12/2011
EP	0164798		12/1985
EP	0453818		10/1991
EP	1018366		12/2000
EP	1097984	A2	5/2001
FR	1546709		11/1968
GB	471186		8/1937
GB	471187		8/1937
GB	471188		8/1937
GB	857086		12/1960
GB	1134585		11/1968
GB	1381619		1/1975
GB	1548277		7/1979
JP	54-079207		6/1979
JP	S54-135712		10/1979
JP	08-119885		5/1996
JP	2001-151708		6/2001
JP	2001-213820		8/2001
JP	2006-272267		10/2006
JP	2007-021396		2/2007
JP	2008-063314		3/2008
JP	2009-000592		1/2009
JP	2009-046653		3/2009
JP	2011-144148		7/2011
LU	52247		12/1966
SU	899523		1/1982
WO	0138271		5/2001
WO	0138275		5/2001
WO	2005016509		2/2005
WO	2007079431		7/2007
WO	2007079435		7/2007
WO	2007096383		8/2007
WO	2009015304		1/2009
WO	2009067571		5/2009
WO	2009087423		7/2009
WO	2011060211		5/2011

(56) **References Cited**

FOREIGN PATENT DOCUMENTS

WO	2011065574	6/2011
WO	2012011844	1/2012
WO	2012081482	6/2012
WO	2012166393	12/2012

OTHER PUBLICATIONS

Boualy et al, "Kharasch Addition of Tetrachloromethane to Alkenes Catalyzed by Metal Acetylacetonates", Catalysis Communications, 2011, pp. 1295-1297, vol. 12.

Chai et al., "Study of Preparation of 1,1,1,3-tetrachloropropane", Zhejiang Chemical Industry, 2010, pp. 1-3, 41(5).

Cristiano et al., "Tetraalkylphosphonium Trihalides. Room Temperature Ionic Liquids as Halogenation Reagents", J. Org. Chem., 2009, pp. 9027-9033, vol. 74.

Evstigneev et al., "Initiated Chlorination of Tetrachloropropane", Khim. Prom., 1984, pp. 393-394, 16(7).

Galitzenstein et al., "The Dehydrochlorination of Propylene Dichloride", Journal of the Society of Chemical Industry, 1950, pp. 298-304, vol. 69.

Gault et al., "Chlorination of Chloroform", Comptes Rendus Des Seances De L'Academie des Sciences, 1924, pp. 467-469, vol. 179.

Gerding et al., "Raman Spectra of aliphatic chlorine compounds II. Chloroethenes and Chloropropenes", Recueil, Jan. 1, 1955, pp. 957-975, vol. 74.

Hatch et al., "Allylic Chlorides. XV. Preparation and Properties of the 1,2,3-Trichloropropenes", JACS, Jan. 5, 1952, pp. 123-126, 74(1).

Hatch et al., "Allylic Chlorides. XVIII. Preparation and Properties of 1,1,3-tricholoro-2-fluoro-1-propene and 1,1,2,3- tetrachloro-1-propene", JACS, Jul. 5, 1952, pp. 3328-3330, 74(13).

Herzfelder, "Substitution in the Aliphatic Series", Berichte der Deutschen Chemischen Gesellschaft, May-Aug. 1893, pp. 1257-1261, 26(2).

Ivanov et al., "Metal Phthalocyanine-Catalyzed Addition of Polychlorine-Containing Organic Compounds to C=C Bonds", Russian Chemical Bulletin, International Edition, Nov. 2009, pp. 2393-2396, 58(11).

Kang et al., "Kinetics of Synthesis of 1,1,1,3,3-pentachlorobutane Catalyzed by Fe-FeCl3", Chemical Research and Application, Jun. 2011, pp. 657-660, 23(6).

Kharasch et al., "Chlorinations with Sulfuryl Chloride. I. The Peroxide-Catalyzed Chlorination of Hydrocarbons", JACS, 1939, pp. 2142-2150, vol. 61.

Khusnutdinov et al., "CCI4 Attachment to Olefins Catalyzed by Chromium and Ruthenium Complexes. Impact of Water as a Nucleophilic Admixture", Oil Chemistry, 2009, pp. 349-356, vol. 4.

Kruper et al., "Synthesis of alpha-Halocinnamate Esters via Solvolytic Rearrangement of Trichloroallyl Alcohols", J. Org. Chem., 1991, pp. 3323-3329, vol. 56.

Leitch, "Organic Deuterium Compounds: V. The chlorination of propyne and propyne D-4", Canadian Journal of Chemistry, Apr. 1, 1953, pp. 385-386, 30(4).

Levanova et al., "Thermocatalytic Reactions of Bromochloropropanes", Russian Journal of Physical Chemistry, Jan. 1, 1983, pp. 1142-1146, vol. 57.

Liu et al., "Progress in the Synthesis of 1,1,1,3-tetrachloropropane", Guangzhou Chemicals, 2011, pp. 41-42, 39(5).

McBee et al., "Utilization of Polychloropropanes and Hexachloroethane", Industrial and Engineering Chemistry, Feb. 1, 1941, pp. 176-181, 33(2).

Mouneyrat, "Effect of Chlorine on Propyl Chloride in the Presence of Anhydrous Aluminum Chloride" Bulletin de la Societe Chimique de Paris, Jan. 1, 1899, pp. 616-623, 3(21).

Munoz-Molina et al., "An Efficient, Selective and Reducing Agent-Free Copper Catalyst for the Atom-Transfer Radical Addition of Halo Compounds to Activated Olefins", Inorg. Chem., 2010, pp. 643-645, 49.

Nair et al., "Atom Transfer Radical Addition (ATRA) of Carbon Tetrachloride and Chlorinated Esters to Various Olefins Catalyzed by CP'Ru(PPh3)(PR3)Cl Complexes", Inorganica Chimica Acta, 2012, pp. 96-103, vol. 380.

Nikishin et al., "Reactions of Methanol and Ethanol", Seriya Khimicheskaya, Dec. 1966, pp. 2188-2192, vol. 12.

Pozdnev et al., "Chlorination of Chloroform and the Conversion of Methylene Chloride Manufacture Still Residues", Khim., Khim. Tekhnol., 1970, 70(4).

Rotshtein et al., "Isomer Distribution on Chlorination of Chloropropanes", Zhurnal Organicheskoi Khimii, Sep. 1966, pp. 1539-1542, 2(9).

Semenov et al., "Selectivity of Photochemical Chlorination of Chloromethane in the Liquid Phase", Zhurnal Prikladnoi Khimii, Apr. 1985, pp. 840-845, 58(4).

Shelton et al., "Addition of Halogens and Halogen Compounds to Allylic Chlorides. I. Addition of Hydrogen Halides", Journal of Organic Chemistry, Sep. 1958, pp. 1876-1880, vol. 23.

Skell et al., "Reactions of BrCl with Alkyl Radicals", Tetrahedron Letters, 1986, pp. 5181-5184, 27(43).

Skell et al., "Selectivities of pi and sigma-Succinimidyl Radicals in Aubstitution and Addition Reactions. Appendix: Response to Walling, El-Taliawi and Zhao", JACS, Jul. 1, 1983, pp. 5125-5131, 105(15).

Tanuma et al., "Partially Fluorinated Metal Oxide Catalysts for a Friedel-Crafts-type Reaction of Dichlorofluoromethane with Tetrafluoroethylene", Catalysis Letters, 2010, pp. 77-82, vol. 136.

Urry et al., "Free-Radical Reactions of Diazomethane with Reactive Bromopolychloroalkanes", JACS, May 5, 1964, pp. 1815-1819, 86(9).

Wang, "Elimination Reactions of Polyhalopropanes under Emulsion Catalytic Conditions to give Halopropenes", Synthesis, Jun. 1982, pp. 494-496, vol. 6.

Zhao et al., "Research Progress on Preparation Technology of 1,1,2,3-Tetrachloropropene", Zhejiang Chemical Industry, 2010, pp. 8-10, 41(8).

Zheng et al., "Review of the Preparation of the low GWP alternative 1,3,3,3-tetrafluoropropene", Zhejiang Chemical Industry, 2010, pp. 5-7, 41(3).

Stevens, "Some New Cyclopropanes with a Note on the Exterior Valence Angles of Cyclopropane", JACS, Vo. 68, No. 4, 1945, 620-622.

Fields et al., "Thermal Isomerization of 1,1-dichlorocyclopropanes", Chemical Communications (London) No. 21, Jan. 1, 1967, p. 1081.

Nguyen et al., "Condensation de chloroforme avec des olefins fluourees en milieu basique", Journal of Flourine Chemistry, vol. 55, No. 3, Dec. 1, 1991, pp. 241-248.

Tobey et al., Pentachlorocyclopropane 1, Journal of the American Chemical Society, vol. 88, No. 11, Jun. 1, 1996, pp. 2478-2481.

Ochi, et al., "Preparation of Chloropropenes by Photochemical Dehydrochlorination of 1,2-Dichloropropane", Chemical Abstracts, Jul. 17, 1989, p. 574, 111(3).

PROCESS FOR THE PRODUCTION OF CHLORINATED ALKANES

This application is a 371 of PCT/US2012/064792, filed Nov. 13, 2012, which claims benefit of 61/562,025, filed Nov. 21, 2011.

FIELD

The present invention relates to processes for the production of chlorinated alkanes, and in particular, to processes for the production of tri-, tetra- and pentachlorinated alkanes.

BACKGROUND

Hydrofluorocarbon (HFC) products are widely utilized in many applications, including refrigeration, air conditioning, foam expansion, and as propellants for aerosol products including medical aerosol devices. Although HFC's have proven to be more climate friendly than the chlorofluorocarbon and hydrochlorofluorocarbon products that they replaced, it has now been discovered that they exhibit an appreciable global warming potential (GWP).

The search for more acceptable alternatives to current fluorocarbon products has led to the emergence of hydrofluoroolefin (HFO) products. Relative to their predecessors, HFOs are expected to exert less impact on the atmosphere in the form of a lesser, or no, detrimental impact on the ozone layer and their lower GWP as compared to HFC's. Advantageously, HFO's also exhibit low flammability and low toxicity.

As the environmental, and thus, economic importance of HFO's has developed, so has the demand for precursors utilized in their production. Many desirable HFO compounds, e.g., such as 2,3,3,3-tetrafluoroprop-1-ene or 1,3,3,3-tetrafluoroprop-1-ene, may typically be produced utilizing feedstocks of chlorocarbons, and in particular, highly chlorinated alkanes, e.g., tri-, tetra- and pentachloroalkanes.

Unfortunately, these higher chlorides have proven difficult to manufacture using acceptable process conditions and in commercially acceptable regioselectivities and yields. For example, conventional processes for the production of trichloropropane (such as those disclosed in U.S. Pat. No. 2,119,484 and U.S. Pat. No. 4,051,182) provide unacceptable selectivity to the desired trichloropropane isomer, make use of suboptimal chlorinating agents, and/or require the use of expensive catalyst systems and/or initiators.

It would thus be desirable to provide improved processes for the production of chlorocarbon precursors useful as feedstocks in the synthesis of refrigerants and other commercial products. More particularly, such processes would provide an improvement over the current state of the art if they provided a higher regioselectivity relative to conventional methods, made use of optimal chlorinating agents and/or made use of less expensive catalyst systems and/or initiators.

BRIEF DESCRIPTION

The present invention provides efficient processes for the production of chlorinated alkanes. More particularly, the processes make use of one or more mono- and/or dichloroalkanes to produce tri-, tetra-, and pentachloroalkanes with high selectivity. In some embodiments, the processes advantageously make use of 1,2-dichloropropane, a by-product in the production of chlorohydrin, as a low cost starting material. Selectivity of the process is enhanced over conventional chlorination processes by employing a Lewis acid as an ionic chlorination catalyst, instead of the catalyst systems comprising multiple catalysts required by the conventional processes. Further cost savings are provided in that low intensity process conditions, e.g., low temperatures, ambient pressure and minimal reactor residence time, are utilized.

In one aspect, the present invention provides a process for the production of tri-, tetra, and/or pentachlorinated alkanes from one or more mono and/or dichlorinated alkanes. The process comprises chlorinating the one or more mono and/or dichlorinated alkane in the presence of one ionic chlorination catalyst. In some embodiments, the mono and/or dichlorinated alkane is a vicinal dichlorinated alkane, e.g., a 1,2-dichloroalkane, and in such embodiments, the corresponding trichlorinated alkane, e.g., a 1,1,2-trichloroalkane, may be produced with a regioselectivity of at least 20:1, or at least 30:1, or at least 40:1, or even at least 50:1. In some embodiments, the dichlorinated alkane may be 1,2-dichloropropane and the trichlorinated alkane may be 1,1,2-trichloropropane. The chlorinating agent is desirably a liquid, and in some embodiments, may desirably be sulfuryl chloride. The ionic chlorination catalyst is desirably a Lewis acid catalyst, such as aluminum chloride, and advantageously, the process requires only the use of one such catalyst. The process is desirably conducted at low intensity conditions, e.g., a reaction temperature of from 55° C. to 65° C., ambient pressure, and with a reactor residence time of 1 hour or less.

DETAILED DESCRIPTION

The present specification provides certain definitions and methods to better define the present invention and to guide those of ordinary skill in the art in the practice of the present invention. Provision, or lack of the provision, of a definition for a particular term or phrase is not meant to imply any particular importance, or lack thereof. Rather, and unless otherwise noted, terms are to be understood according to conventional usage by those of ordinary skill in the relevant art.

The terms "first", "second", and the like, as used herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another. Also, the terms "a" and "an" do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item, and the terms "front", "back", "bottom", and/or "top", unless otherwise noted, are merely used for convenience of description, and are not limited to any one position or spatial orientation.

If ranges are disclosed, the endpoints of all ranges directed to the same component or property are inclusive and independently combinable (e.g., ranges of "up to 25 wt. %, or, more specifically, 5 wt. % to 20 wt. %," is inclusive of the endpoints and all intermediate values of the ranges of "5 wt. % to 25 wt. %," etc.). As used herein, percent (%) conversion is meant to indicate change in molar or mass flow of reactant in a reactor in ratio to the incoming flow, while percent (%) selectivity means the change in molar flow rate of product in a reactor in ratio to the change of molar flow rate of a reactant.

Reference throughout the specification to "one embodiment" or "an embodiment" means that a particular feature, structure, or characteristic described in connection with an embodiment is included in at least one embodiment. Thus, the appearance of the phrases "in one embodiment" or "in an embodiment" in various places throughout the specification is not necessarily referring to the same embodiment. Further, the particular features, structures or characteristics may be combined in any suitable manner in one or more embodiments.

Throughout the specification, "PDC" may be used herein as an abbreviation for 1,2-dichloropropane and "TCP" may be used as an abbreviation for 1,2,3-trichloropropane.

The present invention provides efficient processes for the production of chlorinated alkanes. The present processes comprise reacting one or more mono- and/or dichloroalkanes to tri-, tetra- and/or pentachloroalkanes, with high regioselectivity, e.g., to 1,1,2-trichloroalkanes, 1,2,2,3-tetrachloropropane and/or 1,1,2,2,3-pentachloropropane. Advantageously, only one catalyst is required, and desirably comprises a Lewis acid catalyst. Furthermore, the present processes make use of sulfuryl chloride as a chlorinating agent, rather than a gaseous chlorinating agent such as chlorine gas. The use of sulfuryl chloride is not only advantageous in that it is easier to transport and utilize than gaseous chlorinating agents, but also because, since it is a liquid, it can also serve as a solvent for the reaction and desired catalyst. Finally, the process uses lower intensity process conditions than at least some conventional processes, and thus, operating costs are saved.

The present process can make use of one or more mono- and/or dichlorinated alkanes to produce the desired tri-, tetra- and or pentachlorinated alkanes. Desirably, at least one of the chlorinated alkanes is a vicinal dichlorinated alkane, i.e., the chlorine atoms are present on adjacent carbon atoms. The use of vicinal dichlorinated alkanes is advantageous in that it contributes to the regioselectivity provided by the process.

Any alkane can be utilized in the process, although alkanes comprising from 2-10 carbon atoms, or from 2-8 carbon atoms, or from 2-6 carbon atoms, or from 2-5 carbon atoms, or from 2-4 carbon atoms, or from 2-3 carbon atoms, are particularly suitable. In some embodiments, one of the mono- and/or dichlorinated alkanes comprises mono- or dichlorinated propane, and in those embodiments wherein the dichlorinated alkane is desirably vicinal, comprises 1,2-dichloropropane. The use of 1,2-dichloropropane as a feedstock for the process is advantageous, since it may be available at low cost due to its production as a by-product in many chlorohydrin processes. The one or more mono- and/or dichlorinated alkanes may be generated within the process, if desired, by any methods known to those of ordinary skill in the art.

The tri-, tetra-, and/or pentachlorinated alkane produced by the process will depend upon the mono- and/or dichlorinated alkane used as a starting material, and so, in some embodiments, and due to the commercial significance of trichlorinated ethanes, propanes and butanes, the use of one or more mono and/or dichlorinated ethanes, propanes and butanes as starting materials may be preferred. In some embodiments, 1,2-dichloropropane is utilized as a starting material to produce 1,1,2-trichloropropane at high selectivity, while in others a combination of monochloropropane and 1,2-dichloropropane is utilized as a starting material to produce 1,2,2,3-tetrachloropropane and/or 1,1,1,2,3-pentachloropropane and 1,1,2,2,3-pentachloropropane.

The one or more chlorinated alkane is advantageously chlorinated using a liquid chlorinating agent, such as sulfuryl chloride. The use of a liquid chlorinating agent is advantageous compared to the use of a gaseous chlorinating agent, such as chlorine gas, since a liquid is easier to transport and/or handle than a gaseous chlorinating agent. Chlorine gas in particular, can present a safety hazard. Liquid chlorinating agents, and in particular, sulfuryl chloride (SO_2Cl_2), can also act as a solvent for certain catalyst systems and/or reactions, thereby assisting in the provision of an acceptable reaction rate and/or yield. And so, in some embodiments, sulfuryl chloride may desirably be used as the chlorinating agent.

The specificity of the process is further enhanced by the use of a Lewis acid as an ionic chlorination catalyst. It has now been surprisingly discovered that, e.g., anhydrous aluminum chloride, although known as a component of a multicatalyst system for the chlorination of alkanes, when used alone, assists in providing a high degree of specificity to the desired tri-, tetra- and/or pentachloroalkane, e.g., a 1,1,2-trichloroalkane, 1,2,2,3-tetrachloropropane and/or 1,1,2,2,3-pentachloropropane. More particularly, aluminum chloride has conventionally been utilized with at least one other catalyst, oftentimes iodine and/or ferric chloride, as a component of a free radical initiator system that often requires the additional use of an initiator, such as ultraviolet light. In contrast, the present inventors have now discovered that aluminum chloride may be used as an ionic chlorination catalyst, and in combination with sulfuryl chloride as a chlorinated agent, acts to transform one or more mono- and/or dichloroalkanes, which in some embodiments may comprise a vicinal dichloroalkane, to the corresponding 1,1,2-trichloroalkane, 1,2,2,3-tetrachloropropane and/or 1,1,2,2,3-pentachloropropane with regioselectivities of greater than 10:1, or greater than 20:1 or greater than 30:1 or even at a 40:1 ratio, or greater, over other tri-, tetra- and pentachloroalkane products.

Generally speaking, enough of the catalyst should be utilized to provide some improvement to reaction process conditions (e.g., a reduction in required temperature) and desirably, reaction selectivity, but yet not be more than will provide any additional benefit, if only for reasons of economic practicality. For purposes of illustration only, then, it is expected that useful concentrations of anhydrous aluminum chloride will range from 0.01% to 20% by weight each with respect to the mono and/or dichlorinated alkane(s), or from 0.1% to 10%, or from 1% to 5 wt. %, inclusive of all subranges there between.

The reaction conditions under which the process is carried out are advantageously low intensity. That is, low temperatures, e.g., of less than 100° C., or less than 90° C., or less than 80° C. or less than 70° C., or less than 60° C., or less than 50° C., or even as low as 40° C. may be utilized and the desired selectivities to the tri-, tetra-, and/or pentachloroalkanes yet be realized. In some embodiments, temperatures of from 40° C. to 70° C., or 55° C. to 65° C. may be utilized. Similarly, ambient pressure is suitable for carrying out the process, or pressures within 250, or 200, or 150, or 100, or 50, or 40, or 30, or 20, or even 10 psi, of ambient are suitable. Reactor occupancy may also be minimized with the desired selectivities yet seen—for example, reactor occupancy times of less than 20 hours, or less than 15 hours, or less than 10 hours, or less than 5 hours, or less than 4, 3, 2, or even 1 hour, are possible. The reactor may be any suitable liquid phase reactor, such as a batch or continuous stirred tank autoclave reactor with an internal cooling coil. A shell and multitube exchanger followed by vapor liquid disengagement tank or vessel can also be used.

In one exemplary process, 1,2-dichloropropane is converted to 1,1,2-trichloropropane at selectivities of, e.g., 40:1 over other trichloroalkane products, by reacting 1,2-dichloropropane with sulfuryl chloride in the present of aluminum chloride at a temperature of from 55° C. to 65° C., ambient pressure and a reactor occupancy of less than one hour.

In another exemplary process, monochloropropane is converted 1,1,2,2,3-pentachloropropane at selectivities of, e.g., 40:1 over other trichloroalkane products, by reacting monochloropropane with sulfuryl chloride in the presence of aluminum chloride at a temperature of from 55° C. to 65° C., ambient pressure, and a reactor occupancy of 24-48 hours.

Some embodiments of the invention will now be described in detail in the following examples.

Example 1

Ionic Chlorination of PDC to TCP Using Aluminum Chloride as Catalyst and Sulfuryl Chloride as Chlorinating Agent

Liquid sulfuryl chloride and PDC (1,2-dichloropropane) are mixed in a 100 ml flask heated in a water bath to maintain temperature 55° C.-60° C. in the presence of aluminum chloride ($AlCl_3$) catalyst. A reflux column is placed to return unreacted reactants as well the reaction intermediate 1-chloropropene to the reaction liquid while the HCl and SO_2 byproducts are released to a caustic scrubber at the top of the reflux column. Gas chromatography coupled with mass spectroscopy is used to determine the product composition.

After 30 minutes of reaction time in 40 mole % of $AlCl_3$ the product mixture was found to be 1,1,2-trichloropropane and 1,2,3-trichloropropane at molar ratio of 40 to 1.

Example 2-Comparative

Chlorination of PDC to TCP Using Aluminum Chloride as Catalyst and Chlorine Gas as Chlorinating Agent

Liquid PDC and an inert solvent, carbon tetrachloride, are mixed in a 100 ml flask heated in a water bath to maintain a temperature of 55° C.-60° C. in the presence of $AlCl_3$ catalyst. A reflux column is placed to return unreacted reactants. Gaseous chlorine is bubbled into the liquid phase. Gas chromatography coupled with mass spectroscopy is used to determine the product composition.

After 60 minutes of reaction time in 10 mole % of $AlCl_3$ the product mixture was found to be 1,1,2-trichloropropane and 1,2,3-trichloropropane at molar ratio of 8 to 1.

Example 3-Comparative

Chlorination of PDC to TCP Using Aluminum Chloride and Iodine as Catalyst and Sulfuryl Chloride as Chlorinating Agent

Liquid sulfuryl chloride and PDC are mixed in a 100 ml flask heated in a water bath to maintain a temperature of 55° C.-60° C. in the presence of $AlCl_3$ and I_2 catalyst. A reflux column is placed to return unreacted reactants. Gaseous chlorine is bubbled into the liquid phase. Gas chromatography coupled with mass spectroscopy is used to determine the product composition.

After 180 minutes of reaction time in 1.2 mole % of $AlCl_3$ and 0.3 mole % of I_2 the product mixture was found to be 1,1,2-trichloropropane and 1,2,3-trichloropropane at molar ratio of 4 to 1.

Example 4

Ionic Chlorination of Monochloropropane to TPC Using Aluminum Chloride as Catalyst and Sulfuryl Chloride as Chlorinating Agent

Liquid sulfuryl chloride and 2-chloropropane are mixed in a 100 ml flask heated in a water bath to maintain temperature 55° C.-60° C. in the presence of $AlCl_3$ catalyst. A reflux column is placed to return unreacted reactants as well the reaction intermediates to the reaction liquid while the HCl and SO_2 byproducts are released to a caustic scrubber at the top of the reflux column. Gas chromatography coupled with mass spectroscopy is used to determine the product composition.

After 120 minutes of reaction time in 40 mole % of $AlCl_3$ the product mixture was found to be 1,1,2-trichloropropane and 1,2,3-trichloropropane at molar ratio of 40 to 1.

Example 5

Ionic Chlorination of PDC to 1,1,2,2,3-Pentachloropropane Using Aluminum Chloride as Catalyst and Sulfuryl Chloride as Chlorinating Agent

Liquid sulfuryl chloride and PDC are mixed in a 100 ml flask heated in a water bath to maintain temperature 55° C.-60° C. in the presence of $AlCl_3$ catalyst. A reflux column is placed to return unreacted reactants as well the reaction intermediates to the reaction liquid while the HCl and SO_2 byproducts are released to a caustic scrubber at the top of the reflux column. Gas chromatography coupled with mass spectroscopy is used to determine the product composition.

After 17 hours of reaction time in 40 mole % of $AlCl_3$ the product mixture was found to be 1,1,2,2,3-pentachloropropane as the only pentachloropropane.

The invention claimed is:

1. A process for the production of tri-, tetra- and/or pentachlorinated alkanes from one or more mono and/or dichlorinated alkanes comprising chlorinating the mono and/or dichlorinated alkane in the presence of aluminum chloride, wherein the chlorinating agent comprises sulfuryl chloride.

2. The process of claim **1**, wherein at least one of the one or more mono- and/or dichlorinated alkanes comprises a vicinal dichloroalkane.

3. The process of claim **1**, wherein the dichloroalkane comprises 1,2-dichloropropane.

4. The process of claim **3**, wherein the tri-, tetra- and/or pentachlorinated alkane comprises a 1,1,2-trichloroalkane.

5. The process of claim **4**, wherein the tri-, tetra- and/or pentachlorinated alkane comprises 1,1,2-trichloropropane.

6. The process of claim **5**, wherein selectivity of the process to 1,1,2-trichloropropane is at least 20:1.

7. The process of claim **6**, wherein selectivity of the process to 1,1,2-trichloropropane is at least 40:1.

8. The process of claim **3**, wherein the tri-, tetra- and/or pentachlorinated alkane comprises a 1,2,2,3-tetrachloroalkane.

9. The process of claim **8**, wherein the tri-, tetra- and/or pentachlorinated alkane comprises 1,2,2,3-tetrachloropropane.

10. The process of claim **3**, wherein the tri-, tetra- and/or pentachlorinated alkane comprises a 1,1,2,2,3-pentachloroalkane.

11. The process of claim **10**, wherein the tri-, tetra- and/or pentachlorinated alkane comprises 1,1,2,2,3-pentachloropropane.

12. The process of claim **1**, wherein the process is conducted at a temperature of from 40° C. to 70° C.

13. The process of claim **1**, wherein the process is conducted at ambient pressure.

14. The process of claim **1**, wherein the process is carried out in a liquid phase reactor, and the reactor residence time is less than 1 hour.

* * * * *